

LETTERS

Polyol Process Synthesis of Monodispersed FePt Nanoparticles

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Monodispersed FePt nanoparticles are synthesized by reduction of iron(II) acetylacetonate and platinum(II) acetylacetonate with 1,2-hexadecanediol as the reducing reagent in the polyol process. As-prepared FePt nanoparticles are chemically disordered with fcc phase. Transmission electron microscopy (TEM) images show a self-assembled particle array with an average particle size of 3 nm and a standard deviation about 10%. The transformation from chemically disordered fcc to chemically ordered L1₀ phase is achieved by annealing at 650 °C for 30 min in Ar atmosphere where the oxygen level is less than 1 ppm. Magnetic hysteresis measurements show a coercivity of 9.0 kOe at 293K, and 16.7 kOe at 5 K for the annealed FePt nanoparticles.

Chemically ordered CoPt and FePt alloys with L1₀ crystalline phase are key candidates for future generation ultrahigh density magnetic recording media, due to their enhanced magnetocrystalline anisotropy and the potential for reduced thermally stable grain sizes.¹ However, synthesis of respective nanostructures with control over size, size distribution, and chemical composition still remains a major challenge. The first successful demonstration of monodispersed FePt nanoparticles has been accomplished by solution phase chemical synthesis.² The reaction is based on the simultaneous thermal decomposition of iron pentacarbonyl and reduction of Pt(II) salt in the presence of surfactant molecules. However, there are disadvantages associated with iron pentacarbonyl, which arise from its physical nature. Iron pentacarbonyl is a highly toxic, highly flammable liquid at room temperature. In addition to the safety handling concerns, the stoichiometry of the FePt particles is difficult to control using this process. This is due to the fact that the reaction temperature is above boiling point of 103 °C of iron pentacar-

bonyl, therefore some iron pentacarbonyl is lost and not incorporated into the FePt alloy nanoparticles.³

It has been demonstrated that the synthesis of CoPt and FePt nanoparticles can be achieved by reduction reactions only, e.g., without using iron pentacarbonyl.^{4–8} Controlled synthesis of high quality FePt nanoparticles has been shown by using superhydride as the reducing reagent.⁴ However, superhydride is also difficult to handle, since it is flammable and corrosive. Polyol process, using polyol or diol as the reducing reagent, has been widely applied to reduce metal salts to metal particles. Polyol processes to reduce platinum and iron acetylacetonates in tetraethylene glycol at 300 °C or ethylene glycol at 195 °C have been reported, and the possibility of directly synthesizing chemically ordered L1₀ FePt by controlling the reaction kinetics of the polyol process has been suggested.^{7,8} However, the quality of nanoparticles was inferior to those obtained by using iron pentacarbonyl and needs improvement to meet the requirements of self-organized magnetic array for magnetic recording.

To overcome these challenges, we have investigated the polyol process synthesis of high quality FePt nanoparticles

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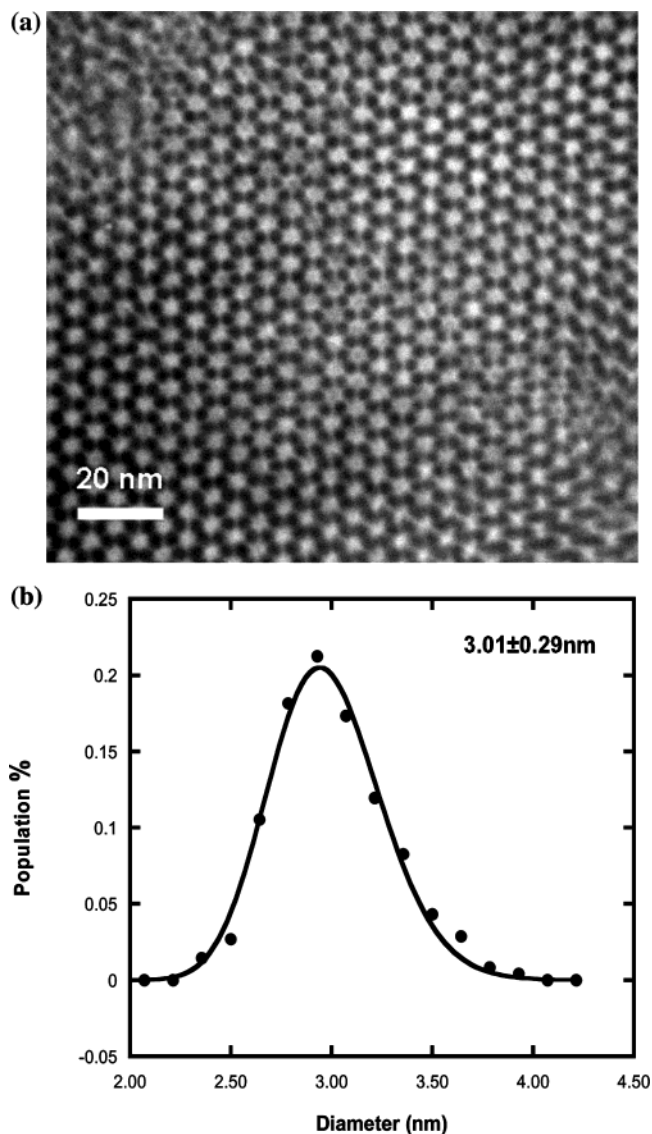


Figure 1. TEM bright field image of as-prepared FePt nanoparticles on the carbon-coated copper grid (a). The particles are monodispersed with a 3.01 nm diameter and standard deviation of 0.29 nm. (b) Curve fitting is based on the assumption of a log-normal distribution.

through the reduction reaction of iron(II) and platinum(II) acetylacetonates by using 1,2-hexadecanediol as the reducing reagent. By utilizing iron salt rather than iron pentacarbonyl, safety concerns are significantly relieved. The chemical composition is accurately controlled by adjusting the relative amounts of Fe(II) and Pt(II) precursors.

All chemicals are used as received. Platinum(II) acetylacetonate (99.99%), iron(II) acetylacetonate (99.95%), oleic acid (90% tech.), oleylamine (70% tech.), octyl ether (99%), anhydrous ethyl alcohol, and hexane are ordered from Sigma-Aldrich. 1,2-Hexadecanediol (90%, tech.) is ordered from Fluka. Since the iron(II) acetylacetonate is a ferrous salt, which can be oxidized in ambient environment, it is handled in a nitrogen glovebox. A standard airless technique has been adapted for the synthesis. A typical experiment begins with mixing stoichiometric amounts of platinum(II) acetylacetonate (0.5 mmol) and iron(II) acetylacetonate (0.5 mmol), reducing reagent 1,2-hexadecanediol (2 mmol), oleic acid (0.5 mmol), and oleylamine (0.5 mmol), in 20.0 mL of octyl ether solution at room temperature. The solution is then heated to reflux at 286 °C and kept at this temperature for 30 min. Afterward, the heat source is removed and the product solution is allowed to cool

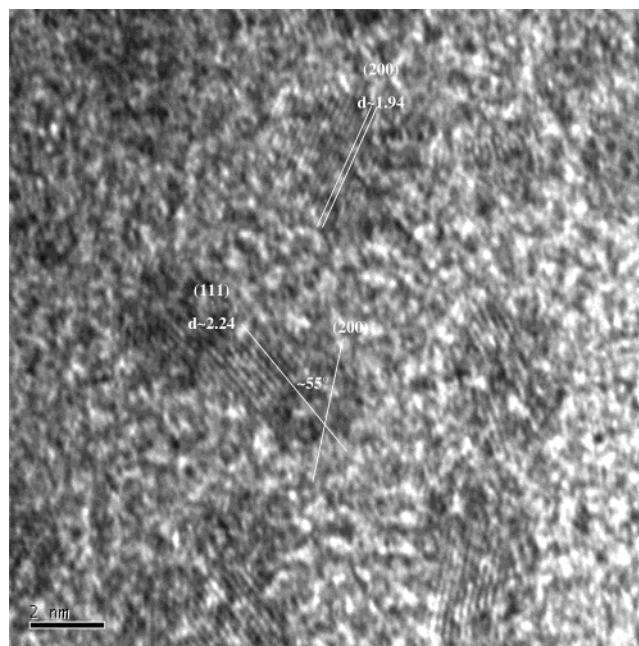


Figure 2. High-resolution TEM image suggests a chemically disordered fcc phase. Identification of random lattice fringes for fcc FePt (111) and (200) planes indicates that the particles are randomly oriented on the TEM grid.

to room temperature. The particle solution is then transferred out of the glovebox. The particles are purified by centrifugation after a flocculent, e.g., ethyl alcohol, is added. The supernatant solution is discarded, and the precipitates are dispersed into nonpolar solvent such as hexane in the presence of oleic acid and oleylamine. The particle solution is dropped onto carbon-coated TEM grids and thermally oxidized Si substrates for characterizations. The solvent is allowed to evaporate slowly (~ 2 – 3 min) by covering with a Petri dish, and the nanoparticle assembly is formed afterward. X-ray diffraction (XRD) studies on the annealed samples are done by a Philips X'PERT PRO MRD equipped with an X-ray mirror using primarily asymmetric glancing incidence scans with the incident angle set at 3 degrees. Conventional TEM studies are carried out using a Philips EM420T microscope operating at 120 kV. High-resolution TEM (HRTEM) studies are carried out using a Philips TECNAI microscope with an operating voltage of 200 kV and a point resolution of 2.1 Å. Magnetic properties are studied with an Oxford Instrument Vibrating Sample Magnetometer (VSM) with 9 T magnetic field capability.

Figure 1(a) shows a bright field TEM image of an as-prepared FePt nanoparticle sample deposited on the carbon-coated grid, verifying that FePt nanoparticles self-organize into superlattices. Figure 1(b) shows a particle size analysis based on a log-normal distribution. The analysis indicates the monodispersity with an average diameter of about 3.01 nm and a standard deviation of about 0.29 nm. A HRTEM image of a similar sample is shown in Figure 2. The images show that the particles have uniform lattice fringes across the particles, which is attributed to good crystallinity of the chemically disordered fcc crystalline phase. Identification of random lattice fringes for fcc FePt (111) and (200) planes indicates that the particles are randomly oriented on the TEM grid. The TEM results are similar to respective results from as-prepared FePt nanoparticles using iron pentacarbonyl chemistry.^{9–10}

It is considered difficult to reduce Fe salt in a polyol process. If there is only iron salt in the reaction system to be reduced by this polyol process, magnetite nanoparticles have been ob-

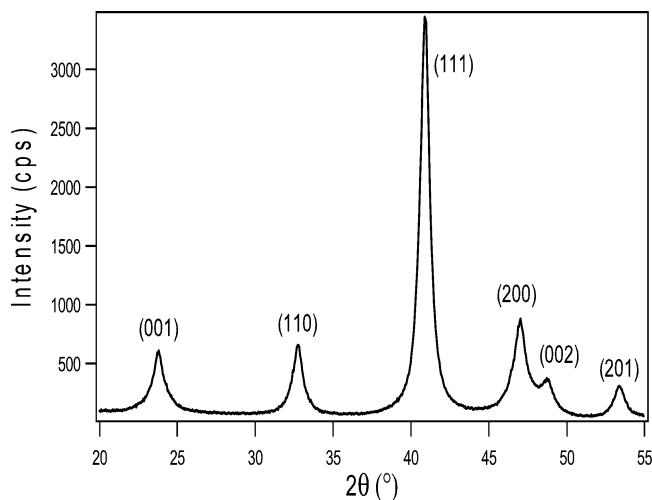


Figure 3. X-ray diffraction pattern of FePt nanoparticles after heat treatment by RTP at 650 °C for 30 min, verified the chemically ordered L_{10} crystalline structure. Profile fitting of the XRD pattern revealed that a is 3.863 Å and c is 3.729 Å, with a c/a ratio of 0.965 by fitting the superlattice (001) and (110) peaks; and a is 3.867 Å, c is 3.742 Å, with a c/a ratio of 0.968 based on the fitting of the fundamental (200)/(002) peaks.

tained.¹¹ The redox potential of the reducing reagent must have a more negative value than that of the metal species. A stronger reducing reagent is needed for the reduction of more electronegative metals. However, it is reported that Pt cations can play a critical role in inducing and accelerating the reduction of associated metal cations.^{7–8,12} The fcc nature of the as-prepared FePt alloy nanoparticles as shown in the HRTEM image in Figure 2 suggests that Fe(II) and Pt(II) precursors are reduced at comparable rates, even though the standard reduction potential for Fe^{2+}/Fe and Pt^{2+}/Pt differ significantly. The reaction mechanism of this polyol process, which may give more insight into the nucleation and growth process of the particles, needs to be more carefully investigated for better quality control.

The transformation from as-prepared chemically disordered fcc to the chemically ordered L_{10} phase is achieved using a rapid thermal processor (RTP) at 650 °C for 30 min in Ar atmosphere. The oxygen level during annealing is less than 1 ppm. An XRD pattern of the annealed FePt nanoparticles having a chemically ordered L_{10} crystal structure is shown in Figure 3. To measure the lattice parameters (both c and a), the superlattice peaks of (001) and (110) are fitted and used to calculate the c -parameter and a -parameter, respectively. Additionally the (200)/(002) peak is de-convoluted and used to calculate the c and a lattice parameters. Profile fitting of the superlattice (001) and (110) peaks of the X-ray diffraction pattern reveals that the lattice constants are $a = 3.863$ Å and $c = 3.729$ Å, with $c/a = 0.965$; they are $a = 3.867$ Å, $c = 3.742$ Å, and $c/a = 0.968$ when fitting the fundamental (200)/(002) peaks. This is consistent with the lattice constants for near-equiatomic FePt bulk material with L_{10} phase.¹³ The measured c/a of 0.965 and 0.968 for our samples is consistent with the fully ordered (order parameter = 1) L_{10} phase. The chemical ordering parameter is close to 1 as the c/a ratio is approximately close to that of equilibrium FePt. Magnetic in-plane hysteresis measurements (Figure 4) show a coercivity (H_c) of 16.7 kOe at 5 K for the annealed FePt nanoparticles, indicating that FePt

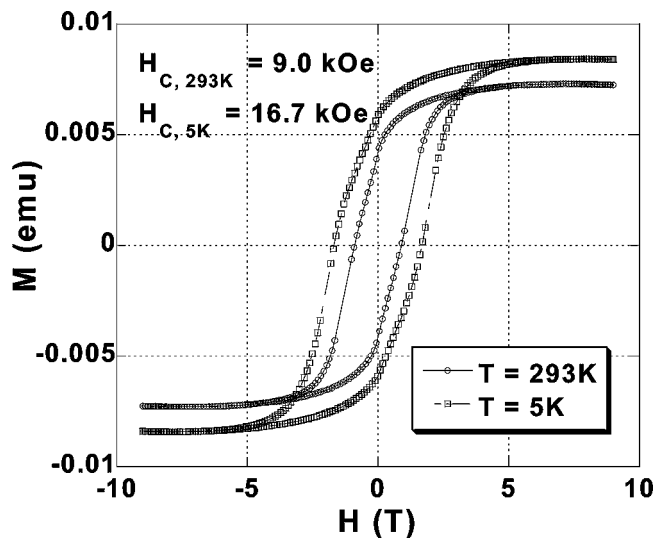


Figure 4. Magnetic in-plane hysteresis measurements of FePt particles after annealing. Coercivities are 9.0 kOe at 293 K and 16.7 kOe at 5 K.

nanoparticles with high anisotropy (L_{10} phase) have been obtained. Both XRD and magnetic property studies verify the transformation from as-prepared chemically disordered fcc to chemically ordered L_{10} phase.

In summary, we have shown that monodispersed FePt nanoparticles are synthesized by reduction of iron(II) acetylacetonate and platinum(II) acetylacetonate by using 1,2-hexadecanediol as the reducing reagent in the polyol process. The as-prepared FePt nanoparticles are chemically disordered with the fcc phase. The transformation from a chemically disordered fcc to chemically ordered L_{10} phase is achieved by annealing at 650 °C for 30 min in Ar atmosphere where the oxygen level is less than 1 ppm. Magnetic hysteresis measurements show a coercivity of 9.0 kOe at 293 K, and 16.7 kOe at 5 K for the annealed FePt nanoparticles. This polyol process provides an alternative approach to synthesize monodispersed FePt nanoparticles safely. Additionally, this process can be extended to other iron-based alloy particle systems such as FePd, FeCoPt, FePt–Ag, etc. Such studies could facilitate the development of magnetic nanoparticles for self-organized magnetic array (SOMA) media.

References and Notes

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